1995 R&D 100 Joint Entry

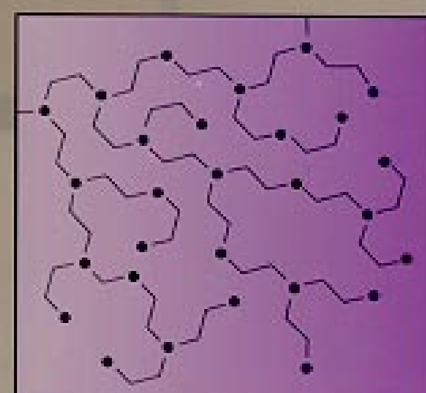
Polymer Filtration (PF) System

Los Alamos National Laboratory
and Boeing Defense and Space Group

Recovers and recycles electroplating metals

No hazardous sludge formation

Compact and efficient



Los Alamos
NATIONAL LABORATORY

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ABOUT THE COVER:

The Polymer Filtration (PF) System was developed to recover zinc and nickel ions from electroplating rinse waters but also can be applied to a variety of other metal-bearing waste streams. The PF unit is mobile, weighs less than 100 pounds, and is capable of pumping 5 gallons a minute. Two key components are (1) a water-soluble, metal-binding polymer, which is added to the unit's 5-gallon fluid reservoir on the left side of the cart, and (2) the two cylindrical ultrafiltration cartridges on the right side of the cart. Controls for monitoring and regulating pH, flow volume, backpressure, and conductivity can be seen underneath the cart's top shelf In the top inset photo, the ultrafiltration membranes, shaped into hollowfibers, are revealed at the open end of an ultrafiltration cartridge. The bottom inset is a stick model of the PF System's branched polymer.

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Executive Summary

Polymer Filtration (PF) System

Features

The Polymer Filtration (PF) System incorporates advanced metal-ion recovery technology in a compact, cart-size apparatus. Our system

- uses water-soluble, metal-binding polymers in combination with ultrafiltration;
- selectively captures valuable metal ions for direct reuse, preventing the formation of hazardous sludge; and
- easily meets EPA discharge limits, reducing industry liability.

Applications

<u>Current</u>

- Recovering metal ions from electroplating rinse water and recycling them to the original electroplating bath.

<u>Future</u>

- Processing the waste streams from mining operations and acid mine drainage.
- Recovering silver from photofinishing and printing wastes.
- Eliminating trace impurities from municipal waste water.
- Removing toxic metals from drinking water.

Benefits

The Polymer Filtration (PF) System is the next-generation technology for recovering, concentrating, and recycling metal ions from industrial waste water, thereby conserving valuable resources and reducing pollution. In its current application for the electroplating industry, the system can be sized for both large and small operations and can eliminate the formation of at least 50,000 tons of metal-containing sludge a year. Potentially applicable for virtually every field requiring advanced metal recovery techniques, the PF System is a revolutionary process that will affect industry worldwide.

1995 R&D 100 Award Entry Form

1. Submitting organization

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AFFIRMATION: I affirm that all information submitted as part of, or supplemental to, this entry presents a fair and accurate representation of this product.

(Signature) ____

2. Joint submitter

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3. Product name

Polymer Filtration (PF) System

4. Brief product description

The Polymer Filtration (PF) System is a new technology for recovering and recycling metal ions from electroplating waste water. The system combines water-soluble polymers that are specially formulated to bind with specific metal ions and a compact pumping and ultrafiltration apparatus that places the polymer in contact with the waste stream and performs the separation. This combination captures, concentrates, and recovers metal ions for reuse.

5. Eligibility: When was this product first marketed or available for order?

Month	May
Year	1994

6. Principal developer	Name: Dr. Barbara F. Smith Position: Technical Staff Member Organization: Los Alamos National Laboratory Phone: (505) 667–2391 FAX: (505) 665–4737

7. Product price
Proprietary

$15,000 per processing unit (estimated)
Dependent on size—The PF unit will be sized to waste stream characteristics: metal amounts, impurity variability, and gallons per minute that require treatment. This estimated price—based on a unit sized to treat 2–4 gallons a minute at a pressure of 25 pounds per square inch—is competitive with, for example, ion exchange technology, which also is sized to a waste stream.

8A. Do you hold any patents on this product?

NO

8B. Do you have any patents pending?

YES
New Polymeric Materials, DOE No. S-78,350
Water-Soluble Polymers for Recovery of Metal Ions from Aqueous Streams, DOE No. S-78,353

8C. Do others in the industry hold patents on this product or a similar product line?

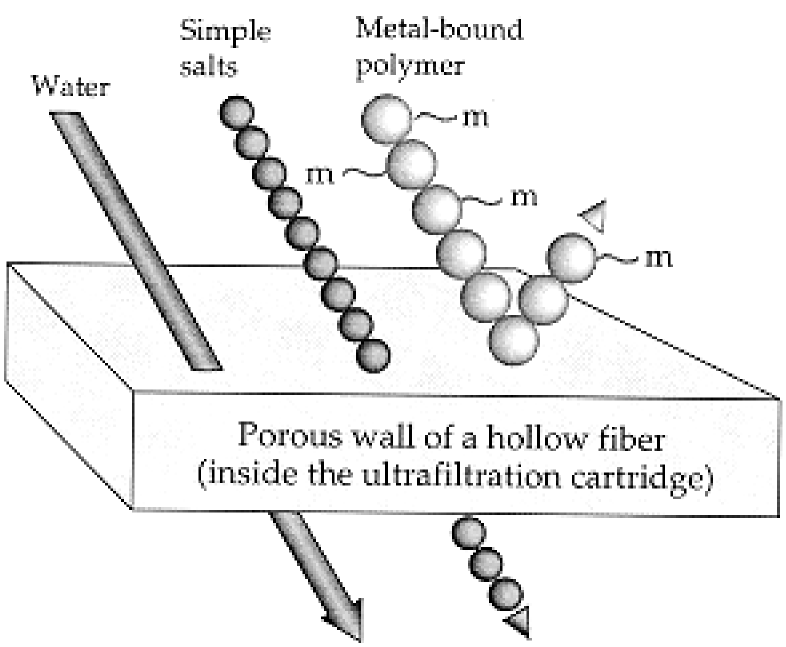
NO

9. Primary function

In electroplating—depositing a protective coating of metal on an object—the item to be treated is first passed through an electroplating bath of metal ions in solution and then washed in a series of rinsing baths. Traditionally, when the process is complete, the electroplating metals that remain in the rinse water are precipitated, collected, and buried as toxic sludge. The sludge is both a waste of valuable electroplating materials and a potential environmental hazard. Our PF System minimizes electroplating waste by recovering the metal ions directly from a processing stream and recycling them to the electroplating bath, thus eliminating the formation of sludge while easily meeting Environmental Protection Agency (EPA) discharge limits.

The PF System is based on the use of metal-binding, watersoluble polymers and on advanced ultrafiltration membranes. We have synthesized new polymers that bind with nickel and zinc and selectively recover them, and we have taken advantage of more than 10 years of substantial improvements in ultrafiltration membrane technology. Those improvements have led to ultrafiltration membranes that are robust (lasting at least 2 years, if properly maintained) and that have greater acid and base stability, better poresize control, and higher flux rates than ever before. Customers for our technology will receive our new polymers, specially formulated for their waste streams, and the complete PF processing unit: a reaction reservoir, pumps, plumbing, controls, and the advanced ultrafiltration membranes, all mounted on a small cart.

Once the PF unit is in place, metal-bearing waste water is pumped into the unit's pH-controlled fluid reservoir, where the polymer binds with the metal ions in the waste stream. The reservoir fluid is then pumped through the ultrafiltration system—a cartridge packed with ultrafiltration membranes shaped into hollow fibers. (The porous walls of the hollow fibers provide more than 60 square feet of ultrafiltration surface area.) The cartridge is configured in a way that directs the fluid to the insides of the hollow fibers at the inlet. As the fluid travels upward, water and other small molecules— simple salts such as calcium and sodium, for example—pass through the porous membrane walls of the fibers and are discharged through the outlet (see accompanying figure). The polymer, however, is too large to pass through the pores, so it and its bound metal ions become concentrated inside the hollow fibers. At the exit ends of the hollow fibers, the metal-bound polymer, which is capable of binding even more metal ions—it has a high loading capacity—is returned to the fluid reservoir for further metal-ion binding. (See Appendix, Figures 1 and 2.) In this manner 500 gallons of rinse water can be treated and the metal ions concentrated to approximately 1 gallon in 2-3 hours. At the end of the process, the PF System discharges water that easily meets or even improves on EPA discharge limits for controlled metals. In many instances the water even meets drinking water standards for controlled metals, equal to or less than 0.1 parts per million for nickel, for example.



When the polymer is fully loaded (has reached its capacity), an operator activates an automatic pH control system, adding dilute hydrochloric acid to the fluid reservoir. This reduces the pH of the solution and causes the polymer to release its hold on the now highly concentrated metal ions. This step is called regeneration. The concentrate is pumped to the ultrafiltration cartridge, where the metal ions, now detached from the large molecules of the polymer, are flushed with approximately 3 gallons of clean water through the porous walls of the hollow-fiber membranes. The collected solution is recycled to the original electroplating bath. The regenerated polymer remains enclosed in the PF processing unit and is ready to treat more waste water in a semicontinuous, closed-loop process that includes no waste sludge formation. (See technical report in Appendix for a more detailed explanation of the PF process.)

Competitors for our system are other metal recovery and wastewater treatment technologies: ion exchange, reverse osmosis, evaporation, filtration (carbon or sand), and electrorecovery. Chelating ion exchange is the technology most closely aligned with polymer filtration, so our matrix focuses on two chelating ionexchange resins: Rohm & Haas's Amerlite-IRC-718 and Bio-Rad's Chelex 100.

Each comparison marked with an asterisk (*) refers to the following processing scenario: Treatment of 500 gallons of rinse water containing 100 parts per million nickel and 50 parts per million zinc (0.624 pounds total metal ions) in 8 or fewer hours. This scenario does not include any other ions that may be in the bath— ammonium chloride or boric acid and traces of copper or iron, for example. The PF recycle unit is compared with an ion-exchange unit developed for point-source metal recovery and available from NAPCO, Inc.

The comparison matrix follows on p. 6.

Parameters	PF System (chelating polymer)	IRC-718 (chelating resin)	Chelex 100 (chelating resin)	Comments
Amount of Binding Agent Needed for Processing Scenario*	1.6 kg	8.5 kg	23.3 kg	The amounts given for resins are company quotes.
Cost of Binding Agent per kg*	$20	$20	$210	The costs given for the two resins are company quotes. The polymer and both resins are reusable.
Total Cost of Binding Agent*	$32	$170	$4,893	
Regeneration of Binding Agent*	Time: 15–30 min. Regenerated solution: 3–5 gal.	Time: 2–4 h Regenerated solution: 10–15 gal.	Time: 2–4 h Regenerated solution: 10–15 gal.	Regeneration is accomplished within the PF System. Resin systems require separate regeneration units.
Metal Ions Recycled to Plating Bath*	Yes	Not usually	Not usually	PF can readily recover a pure metal-ion concentrate. With resins, recovered volumes are often too large.
Relative Capacity of Binding Agent*	4.3	0.7	1.0	The PF polymer can load 3–8 times as much metal as most resins.
Relative Binding Kinetics	Rapid	Moderate to slow	Moderate to slow	PF binds in one phase; resins bind in two phases.
Metal-Ion Selectivity	High	Medium to high	Medium to high	PF is highly selective because it is specially formulated to target specific metal ions.
Estimated System Cost	**$15,000**	$11,000	$20,000	Please note that the PF System price is proprietary. Prices for the resin systems do not include their separate regeneration units.
System Scale-Up	Very easy	Moderately easy	Moderately easy	For the PF System, scale-up requires only larger ultrafiltration membranes. For resin systems, scale-up requires extra effort to deal with the increased backpressure.
Floor Space Required	2 ft x 3 ft	3 ft x 3 ft	3 ft x 3 ft	Resins require separate regeneration units. Those units at least double the space requirements shown here for resin systems.

10C. Improvements on competitive technologies

Our PF System has many advantages over resin-based ion-exchange technology. The most important advantages are as follows:

- Metal-Ion Recycle—A unique aspect of PF is its ability to recover pure metal-ion concentrate in a small volume and recycle it directly to the original electroplating bath, all in a single unit. The regenerated metal-ion solutions from ion-exchange columns generally are not suitable for direct reuse. A second mode of metal recovery (electrorecovery, for example) is necessary.

- Processing Speed—Binding kinetics are more rapid with the PF System because it occurs in a single, aqueous phase (homogeneous reaction). With chelating ion exchange, two phases are involved: aqueous and solid resin. The metal ions transport from the solution onto the organic resin and then into the resin pores (heterogeneous reaction). This process is relatively slow in both the metal-ion binding and regeneration steps. Thus, column flow rates have to be optimized to allow for slower binding and release. Because of this slowness the amount of regeneration solution required to recover the metal ions is large. PF significantly reduces processing times and process volumes.

- Loading Capacity—Our polymer has a loading capacity 3-8 times greater than that of any chelating ion-exchange resin because it has more binding sites. Chelating resins are organic solids that use some of their chemical structure to maintain mechanical stability, thus leaving fewer binding sites available for the metal ions on a weight basis. Also, resin beads must be large enough to avoid building up hydraulic backpressure in the column. Binding sites at the centers of large beads often are not easily accessed.

- Selectivity—Because our polymers use chelation bonding, we are able to tailor a polymer's structure and chelating groups to select specific metal ions, rejecting benign impurities such as calcium, potassium, and other salts. With PF it is possible to easily develop formulations (mixtures) of polymers with different chelators to recover metal ions and separate them as needed. Chelex 100 and IRC-718 each have only one type of chelator, making them highly selective for fewer metal ions.

- System Size—Our system is compact and fits on a 2- by 3-ft wheeled cart, a special convenience for small electroplating shops. The United States alone has more than 10,000 electroplating shops, many with a shortage of floor space near the electroplating lines. Scale-up is easy, however, so our system can be used in all sizes of shops. Resin ion-exchange equipment requires more space because of its multiple columns of resin beads. Additionally, ion-exchange units designed to treat point-source electroplating lines require more space because they must have separate regeneration units to release and collect the metal ions.

The PF System also improves on other conventional metal recovery processes. In contrast with reverse osmosis, PF is carried out at low pressure (equal to or less than 25 pounds per square inch). Unlike evaporation, PF is a low-temperature and therefore low-energy process. Reverse osmosis and evaporation, as opposed to PF, are nonselective, recovering all waste stream salts and materials, including metal ions that are impurities. Through electrodeposition, electrorecovery is able to selectively recover metals as solids but not as ions in solution. Electrodeposition works best with metals found in high concentration.

11A. Principal applications

The principal application of our PF System is the rapid and selective recovery, concentration, and recycle of the nickel and zinc found in electroplating rinse waters, preventing these metals from being disposed of as sludge. Our system was designed specifically for new alloy baths that Boeing is developing to replace environmentally hazardous cadmium electroplating baths, but the PF System is applicable to most nickel- or zinc-bearing electroplating rinse water.

11B. Other applications

The PF System is versatile. Because the polymer formulation used in the system determines the separations chemistry, changing the polymer formulations results in new systems capable of recovering metal ions from many different electroplating waste streams. The PF System can be applied to waste streams that contain copper, tungsten, lead, cadmium, and chromium. This is particularly important for lead, cadmium, and chromium, whose geologic disposal is controlled by the Resource Conservation and Recovery Act.

11C. Future applications

A natural extension of the PF technology is to silver process streams from photofinishing and printing. (The United States has 500,000 photofinishing establishments.) Considering the convenient size of our system, it is ideal for placement wherever silver-bearing waste water is generated. The PF System also has future applicability for cleaning molybdenum, zinc, copper, and small amounts of hazardous and controlled metal ions from mining waste streams, and it can be particularly helpful in removing iron cyanide from solutions of mining waste. We are already experimenting with a newly formulated polymer that has an affinity for iron bonding. In the future, PF can be made applicable to nuclear waste cleanup, removing actinides from waste and process streams. Of particular interest is the possibility of using the PF System to remove trace levels of metal from drinking waters, contaminated aquifers, and utility water. (Millions of people are exposed annually to lead and other toxic metals in their drinking water.) Incorporation of specially formulated polymers into cellulosic cartridges may one day result in a convenient, inexpensive, in-home water purification system. For analytical purposes, the PF System may eventually be used to determine the type and amount of toxic metal ions in body fluids such as urine, or it may be applied as a preconcentration procedure for ultra-low-level metal analyses.

All of these applications await full development and evaluation of the required polymers, but we are confident that they will be accomplished in the future.

12. Summary

Over the last 30-40 years, thousands of tons of valuable metals, many obtained abroad, have been buried as toxic sludge because the technology to recover them from dilute electroplating waste streams has been unavailable or prohibitively expensive. The cost of this sludge is staggering: valuable metals costing thousands of dollars are lost, and at least 13,000 Btu of energy a year are required to replace them. The PF process—a system that is easily operated (reduced man-hours) and robust (reduced downtime)—offers all metalfinishing businesses a convenient and inexpensive way to recover and recycle plating metals, thus reducing material costs. The system is a valuable economic asset.

Equally important, however, the PF System is also an environmental asset. The United States alone has 10,000 metal finishing shops; by 2010 those shops will be adding at least 50,000 tons of sludge a year to the nation's burden of pollution. The United States already has 1,200 Superfund sites, each with an estimated cleanup cost of $25 million. Elsewhere in the world, environmental concerns have led Germany to ban the use of metals such as cadmium in its electroplating industry. Many countries, such as Mexico and Taiwan, still discharge toxic metals into rivers and oceans.

A new metal recovery technology is needed worldwide for all kinds of industrial and metal-processing streams. Our PF System can address this international need. It can be made available to any size business, and as a combination of off-the-shelf ultrafiltration equipment and custom-formulated polymers, it is both low in cost and highly effective—in the matrix scenario, we recover 99% of targeted metals. It discharges water that is even cleaner than required by EPA regulations. Such characteristics make the PF System a truly pivotal metal-recovery technology for the electroplating industry. In recognition of that fact, five companies recently bid for the opportunity to commercialize our product. We have chosen MicroSet (part of FiberTech Group, Inc.) as our industrial partner and, in collaboration with that company, will present our system at several technology fairs and expositions in the coming months. However, we see the PF System as a quantum step forward for all metal-recovery and recycling businesses, not just electroplating. The future applications are many, and in fact, we have already been contacted by two companies interested in exploiting our system's potential for the treatment of mining and photofinishing waste streams.

Originally developed for one industry—electroplating—the PF System promises to revolutionize many industries. With its special combination of water-soluble polymers (the right molecular size and the right chelators) and newly advanced ultrafiltration membranes, PF is the right technology at the right time. Businesses want to support the bottom line and, at the same time, contribute to a healthy environment. With the PF System, those desires do not conflict; they complement each other.

Organization Data

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Appendix

List of Co-developers
Figure 1: Simplified Schematic of the Polymer Filtration System
Figure 2: Metal Retention as a Function of pH for a Selected Polymer
Technical Report: “Polymer Filtration: A New Technology for Selective Metals Recovery,” to be presented at the American Electroplaters and Surface Finishers Society 1995 Exhibition, SUR/FIN ‘95, Baltimore, Maryland, June 25–28, 1995. (This report will appear in Plating and Surface Finishing, American Electroplaters and Surface Finishers Society, Inc.)
Los Alamos Profile

Six copies of a 5-minute video accompany this entry.

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Funding for development of the PF System was provided by the Department of Energy, Office of Industrial Technology, Industrial Waste Reduction Program.

Figure 1. With our equipment, polymer filtration processing occurs in a closed-loop system. Water from the electroplating rinse bath mixes with a special water-soluble polymer in the fluid reservoir, where the polymer binds with the metal ions in solution. The reservoir fluid is then pumped to the ultrafiltration cartridge, passing first through a macrofilter to remove dust and dirt. At the cartridge inlet point, the fluid is forced into the hollow-fiber ultrafiltration membranes that fill the cartridge. There the water and small molecules pass through the porous walls of the hollow fibers, leaving the large, metal-bound polymer inside to be pumped back to the fluid reservoir to bind more metal ions. The metal-cleansed water that has escaped through the walls of the hollow fibers is flushed from the cartridge and can be discharged to the public sewer system.

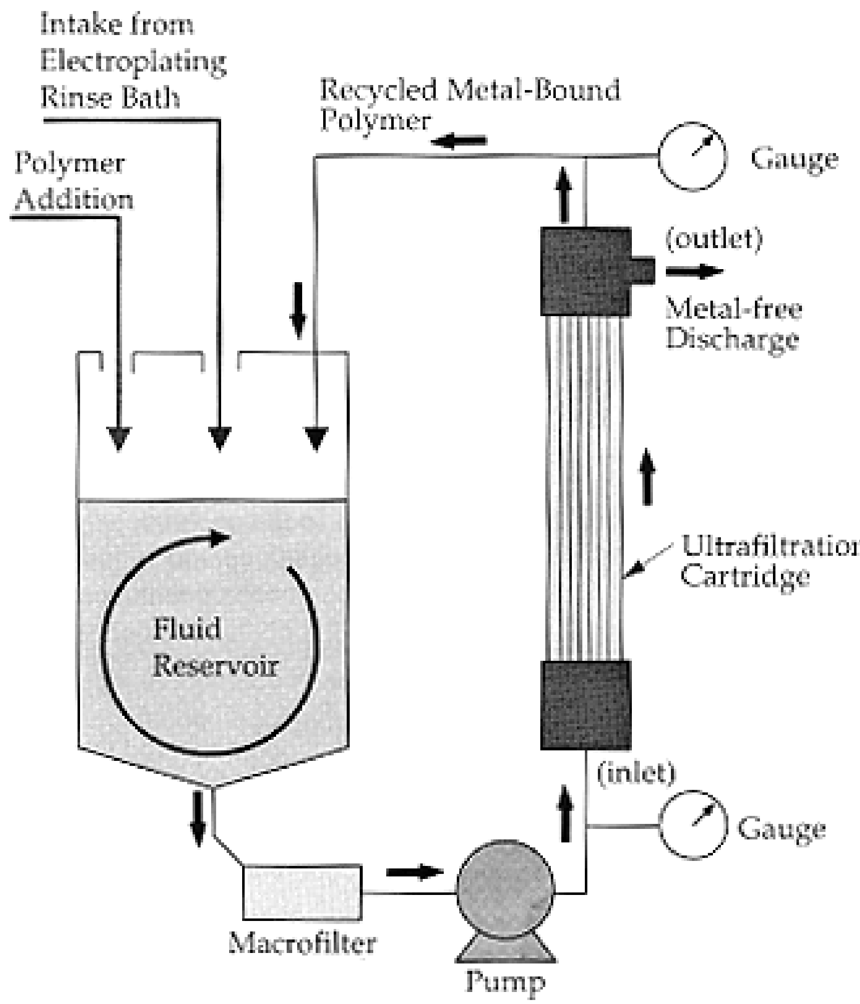

Figure 2. For our specially formulated polymers, metal retention is a function of pH. Metal is loaded at high pH and stripped off (regenerated) at low pH. This graph represents the nickel and zinc retention of one of our polymers, Metal-Set-Z.